DOE Center of Excellence 2001 for the Synthesis and Processing of Advanced Materials

Synthesis and Processing of Carbon-Based Nanostructures

D.M. Gruen, J.A. Carlisle, O. Auciello, D. Mancini, A. Erdemir, S. Phillpot, L. Curtiss *Argonne National Laboratory*	**T. A. Friedman**, M. P. Dugger, J. Sullivan, M. P. DeBoer *Sandia National Laboratory*	E.A. Stach *Lawrence Berkeley National Laboratory*
D. H. Lowndes, V.I.Merkulov *Oak Ridge National Laboratory*	R.J. Nemanich *North Carolina State University*	V.P. Dravid *Northwestern University*

Motivation

Carbon-based materials exhibit unique physical, chemical, mechanical, tribological, and transport properties that are driven by the many different bonding configurations available to carbon. For example, diamond exhibits extreme properties of hardness, atomic density, thermal conductivity, and optical transparency ranging from the far infrared to the near UV. Nanocrystalline diamond films exhibit unique electronic, mechanical, tribological and optical properties induced by the extreme small size of the grains and the grain boundaries. Diamond-like carbon is an amorphous mixture of 4-and 3-fold bonded carbon with properties that can be tailored between graphite and diamond. Fullerene molecules have a unique structure, while carbon nanotubes may be the strongest material in the world and exhibit significant variations in electronic properties for single-walled tubes. Controlled passivation of dangling σ-bonds of surface carbon atoms by hydrogen in diamond and diamondlike carbon films results in superlow friction and wear in sliding bearing applications. Moreover, the surfaces of all of these structures exhibit unusual chemical properties, from the negative electron affinity of diamond, to the chemical stability of diamond, fullerenes and nanotubes. This morphological flexibility makes carbon-based materials inherently multifunctional. In addition, these materials are compatible with inorganic and biological systems, making devices based on carbon materials especially attractive

While silicon has been the basis of modern electronics and the digital revolution, we envision a future with micro and nanotechnologies based on multi-functional carbon materials systems that will enable a second revolution based on microelectromechanical systems (MEMS) and nanoelectromechanical systems (NEMS). We hope to drive these materials into a regime where they can naturally interface both with electronic and biological systems. It is the focus of the proposed Center to explore the fundamental science related to nanostructured carbon-based materials and devices.

Objective

The objective of the proposed Center is to advance the science and technology of carbon-based materials that can result in the development of a new generation of microdevices and microelectromechanical systems (MEMS). The Center's activities are to be focused not only on the development of nanoccomposite carbon-based materials, but also on the science related to their incorporation into nanostructured devices. The Center will thus focus not only on nanoscience but also on the development of *nanoinstrumentation* needed to conduct that science. The overall approach of the Center is to effectively couple existing programs in carbon-based systems. In addition, the proposed Center's research focus will be directly related to a major area of new emphasis in DOE-BES, i.e., the National Nanotechnology Initiative, and also fits in nicely with DOE's plans to support major centers of nanoscience research at several national laboratories.

Scope

Mechanical and Tribological Properties of Carbon-Based Thin Films (SNL, LBNL, ANL, NWU)

When device dimensions shrink to the micro- and nanoscale, actuation forces become quite small as compared to capillary and surface friction forces (stiction). In addition, the devices become much more compliant so that small residual strains can easily distort structures rendering them useless. Thus, understanding, measuring and ultimately controlling mechanical properties of nanostuctured materials presents unique challenges that require novel instrumentation and/or the utilization of novel MEMS architectures (e.g. nanoinstrumentation). The proposed center has unique personal and equipment to perform this characterization.

SNL has extensive facilities in-place for Si and carbon-based MEMS. For example, the Si MEMS foundry with the world's most sophisticated process (SUMMIT) for design and fabrication of five-layer Si MEMS devices. Characterization facilities include an automated interferometric mapping station (IMAP) for wafer level characterization of mechanical properties (friction, stiction, modulus, residual stress, and strain gradients), nanoscale MEMS based friction and wear testing, and pull-tab tensile testing. LBNL has developed a unique integrated TEM/Nanoindenter system to study nanoscale crack formation and defect propagation. We plan to leverage this existing technology to facilitate our efforts and develop new characterization techniques as the program evolves.

Preliminary experiments comparing crack propagation in silicon versus nanocrystalline diamond thin films give striking evidence of the hardness of these films: applied forces that easily give rise to defects in silicon result in no visible effects in nanocrystalline diamond films. The "pull-tab" testing technique developed at SNL has provided invaluable statistical measurements of the fracture strength, modulus, and fracture toughness of poly-Si and amorphous Diamond MEMS, and efforts are currently underway to fabricate a test structure out of nanocrystalline diamond,. TEM studies will be conducted to relate the mesoscale mechnical and tribological properties with film morphology.

The superlow friction and wear mechanisms of diamond and diamond-like carbon films are not yet fully understood, but it is believed that they are associated with hydrogen on the sliding surface. Understanding of the fundamental tribological mechanisms of of these films will be extremely valuable for the design and development of new carbon-based micromachines and related applications. In addition to tribological characterization at SNL and LBNL, computational chemistry will be used at ANL to provide the fundamental information needed to understand the friction and wear mechanisms of these materials.

Electronic Properties of Carbon-Based Materials (ANL, NCSU, NWU, LBNL, SNL)

Electron transport and field emission from nanostructured diamond thin films are two intimately related phenomena that appear to be largely controlled by grain boundary-dominated transport processes and/or field enhancement at localized sites. Recent work at ANL and NCSU has focused on the incorporation of nitrogen into nanocrystalline diamond thin films, with the goal of enhancing their conductivity and emission characteristics. The addition of nitrogen has a tremendous effect on the properties of this material, with conductivities, carrier concentrations, and mobilities approaching that of graphite. TEM work conducted at ANL and NWU has shown that the grain boundaries in nitrogenated films scale with increasing nitrogen concentration. Tight-binding calculations performed at ANL indicate nitrogen segregates to the grain boundaries and that the electronic states in the boundaries can act as electron conduction pathways. The ability to tune the mechanical, electrical, and emission properties of nanocrystalline diamond films via the robust incorporation of nitrogen and other dopants opens whole new areas for the application of these materials.

One unique property of many of these nanostructured carbon materials is robust field emission. Work at NCSU using PEEM has shown that nitrogen-doped, *flat* nanocrystalline diamond thin films exhibit field emission performance comparable to that of other field-enhanced emitters. Another cross-collaboration will address the dependence of the mechanical and tribological properties on doping with nanoinstrumentation developed at SNL and LBNL. It should be emphasized that, without the support of the “glue” money the Center would provide, such efforts would be very difficult to undertake.

Materials Issues in Carbon-based MEMS Devices (SNL, ANL, NCSU, ORNL)

One of the major driving forces for the Center is the recent finding that carbon-based coatings and associated synthesis methods are readily compatible with the familiar silicon-based microelectronics and MEMS processing techniques. In spite of the momentum behind fabrication of Si-MEMS devices, carbon-based MEMS may offer significant advantages owing to the fact that carbon materials have superior wear-resistance and stiction properties. The main barrier to the use of carbon films in MEMS has been the high degree of residual compressive stress in hard films with low hydrogen content. Recent work at ANL and SNL has demonstrated that low stress nanocrystalline and amorphous diamond films can be deposited on various substrates, and that these films can be patterned with oxygen plasma to yield discrete MEMS structures. Stress in the nanocrystalline material is accommodated within the large grain boundary volume and in the amorphous material by diffusionless conversion of a few atomic percent of carbon atoms from 4-fold to 3-fold coordination. Although recent data suggest that these materials have hardness within a few percent of that for single crystal diamond, the mechanisms of fracture and dependence on microstructure are not well understood. Furthermore, the role of adsorption and desorption of environmental species on tribological processes is not known for these materials. Recent work at ORNL has show that carbon-nanofibers and tubes can be grown using the same PECVD techniques used for diamond thin-films, raising the possibility of synthesizing nanocomposites of diamond with carbon nanotubes. These nanocomposites further broaden the range of material properties that could be incorporated into MEMS/NEMS devices. The work performed by the ANL and SNL groups indicate that it may be possible to integrate low stress, high strength diamond structures with an ultralow friction surface layer and dramatically increase the performance and reliability of a new class of microsystems based on carbon.

Carbon-Based Nanocomposites (ORNL, NCSU, ANL, SNL)

Carbon nanotubes display unusual structural and electronic properties as a function of diameter and helicity, showing substantial promise as electron emitters, super-strong fibers, catalysts, hydrogen storage media, batteries, molecular wires, and molecular switches. It is expected that these hybrid carbon nanotube/nanocrystalline diamond structures will exhibit unique electronic and mechanical properties in addition to being the basis for a wide range of biocompatible devices. Both the ANL and ORNL teams have produced carbon nanotubes using similar microwave plasma CVD systems. Aligned carbon nanotubes will be grown using a process capable of producing a regular array of carbon nanotubes. In this method, a porous oxide layer is produced, under certain electro-chemical-thermal conditions, on an appropriate substrate (e.g., Si or glass). This layer yields a remarkably ordered arrangement of cylindrical pores. These nanoscale pores are parallel, straight, oriented vertical to the surface; and they are uniform in diameter and in spacing. Carbon nanotubes will be grown inside the pores using microwave plasma CVD. Combining all this expertise could lead to the development of, for example, ultra small (nanometer scale) electron sources, which could be integrated into MEMS and NEMS for sensor applications. The electron beams could also be used for local light sources or for initiating local chemical reactions. Computational chemistry calculations and molecular dynamics simulations will compliment this experimental work.

Interactions with DOE Technologies and Industry

The project is relevant to the needs of several DOE Technology Offices, including Defense Programs, EE/Transportation Technologies, and Energy Efficiency. Furthermore, some of the groups involved in the Center are already conducting or discussing joint projects with several companies [e.g., UHV Technologies (Illinois), Flow-Serve (Illinois), Second Sight (California)] that are interested in the proposed program and in discussing associations to our proposed Center.

Management Plan

The project coordinators for the Center will be Drs. D.M. Gruen (ANL) and T.A. Friedmann (SNL). The number of participants and institutions was kept to a manageable level, so that each institution will receive support to allow for either a post-doctoral associate (at the national labs) or a graduate student (at the universities). Thus, we envisage the majority of the funds will be used to support four-to-five postdocs and two-to-three graduate students, giving the Center a high educational component. Matching funds from the various institutions and possibly industry will help support these postdocs/students as well. The remaining funds will be used to fund Center Workshops and travel costs to major international conferences.